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Growth and characterization of ZnO nanorods by microwave-assisted route: green chemistry approach

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ABSTRACT

ZnO nanorods with diameter 90-100 nm range (tip diameter~15 nm) and length of about 2 μm have been prepared using microwave irradiation technique. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results indicate that the nanorods have single phase nature with wurtzite structure and preferentially grow along [0001] direction. Raman spectrum shows the mode E_2^{high} at 439 cm^{-1} that is related to the vibration of oxygen atoms in wurtzite ZnO. Room-temperature ultraviolet-visible (UV-vis) absorption spectrum shows the absorption band at around 399 nm (red shifted as compared to bulk). This novel nanostructure would be a promising candidate for a variety of future applications. Copyright © 2011 VBRI press.

Keywords: ZnO; nanorods; TEM; XRD; microwave irradiation.

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Introduction

In the recent years, one-dimensional (1D) nanoscale materials have received considerable attention due to their remarkable properties useful in optoelectronic and electronic nanodevices. [**1, 2**] For understanding the basic concepts of quantum size effect on electrical, optical, mechanical and magnetic properties, some important semiconductor nanomaterials, such as GaN [**3**], CdS [**4**], Si [**5**], SnO_2 [**6**], TiO_2 [**7**] ZnO [**8, 9**] and CeO_2 [**10-13**], have been widely studied and are still in focus. Among them, ZnO 1D nanomaterials such as nanorods, naotubes and nanowires have been intensively chosen due to their remarkable properties such as wide direct-band gap (E_g ~3.4 eV) and large exciton binding energy (60 meV), which allows UV lasing action to occur even at room temperature [**14**]. ZnO with oxygen vacancies exhibits an efficient green emission, leading to a wide variety of potential applications in catalysts, gas sensors, piezoelectric, optoelectronic devices, and solar cells. [**15, 16**] Up to now, ZnO particles with various morphologies, such as nanobelts, nanonails, flower like, tower like, tube like, doughnut like, ellipsoidal, and so on, have been synthesized by various methods, including sonochemical synthesis [**17**], co-precipitation method [**18, 19**], refluxing method [**20**], hydrothermal method [**21**] and vapor

transport process at low temperature [**22**]. Wang's research group has successfully prepared a variety of nanostructures of ZnO, including nanowires, nanorings, nanobelts, nanoribbons, and nanonails, by a vapor–liquid–solid (VLS) process [**23–26**]. Though, most of these routes have engaged high temperature or expensive organic precursor, which are adverse for large-scale production. Among these methods, microwave irradiation has paying interest of researcher's owing to its unique features such as environmental friendly reactions, short reaction time, rapid volumetric heating, energy saving, and high reaction rate [**27, 28**]. Microwave energy transforms into heat inside the material which reduces the energy consumption, decreases the process time and provides rapid and controllable volumetric heating with a particular temperature distribution. Because microwave radiation has the advantages of uniform heating, it is simple to produce homogeneous nucleation, and the precipitate can be rapidly dissolved in aqueous solution to make a saturated solution. In general, the power, heating frequency, and on/off irradiation cycles are the main heating parameters of a microwave oven, and each of them may have a great effect on the structure and properties of the products.

In this paper, we report a simple microwave assisted method to synthesize spear shaped ZnO nanorods (nanoflowers). The synthesized product was characterized by XRD, FESEM, EDX, TEM, UV-vis and Raman spectroscopy measurements. This efficient, cost effective and energy saving method allows the preparation of ZnO nanorods in large quantity. We believe that the presented approach is a simple one to synthesize ZnO nanostructures for the practical application of photo catalysis as well as optoelectronic device applications in which optical properties play a key role.

Experimental

All of the reagents involved in the experiments were of analytical grade and utilized as received without further purification. The synthesis was carried out in a domestic microwave oven (Samsung, 750 W). In a typical synthesis, a 1:20 molar ratio of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$; 99.99%, Sigma Aldrich) to potassium hydroxide (KOH; 99.99%, Sigma Aldrich) was dissolved in 100 ml deionized water in a round-bottom flask, and then put into a domestic microwave oven. Microwave irradiation proceeded at 180 W (irradiation 12 s, stop 10 s) for 15 min. After microwave processing, the solution was cooled to room temperature. The resulted precipitate was separated by centrifugation, then washed with deionized water and absolute ethanol for several times, and finally dried in an oven at 80 °C for 24 h and annealed at 400 °C for 1 h in air.

The phase purity of the as-obtained product was characterized by x-ray diffraction using Phillips X'pert (MPD 3040) x-ray diffractometer with Cu *K*α radiations (λ = 1.5406 Å) operated at voltage of 40 kV and current of 30 mA. Field emission scanning electron microscopy (FESEM) images were obtained using TESCAN; MIRA II LMH microscope. The elemental composition of as prepared ZnO was determined by energy dispersive X-ray spectroscopy (EDX, Inca Oxford, attached to the FESEM). Transmission electron microscopy (TEM) micrographs, selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) images were obtained by a FE-TEM (JEOL/JEM-2100F version) operated at 200 KV. The optical absorption spectrum was recorded in the range of 200–800 nm using a UV-3101PC UV–VIS-NIR scanning spectrometer (Shimadzu, Japan). In order to get the phonon vibrational study of the ZnO nanorod, micro-Raman spectrometer (NRS-3100) was used with a 532 nm solid-state primary laser as an excitation source in the backscattering configuration at room temperature. The incident laser power on samples was less than 10 mW.

Results and discussion

Fig. 1 shows typical XRD pattern of as prepared ZnO, which was indexed as the pure hexagonal phase of ZnO with the lattice parameters a = 3.254 Å and c = 5.197 Å, which were very close to the reported data (JCPDS, 89-0501). XRD pattern was indexed using POWDER-X [**29**] software. It can be clearly seen from the pattern that the sample showed a single-phase nature with a wurtzite structure. No diffraction peaks from any other impurities were detected and the sharpness of the peaks implied the high crystallinity of the as-prepared ZnO nanorods.

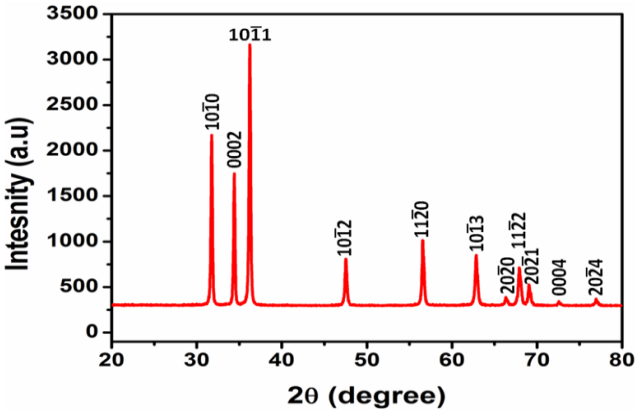

Fig. 1. XRD pattern of the ZnO nanorods.

Fig. 2 represents the morphology of the as-synthesized ZnO nanorods prepared by the microwave irradiation. Typical FESEM images of the ZnO nanostructures at two different magnifications are shown in Fig. 2(*a*) and (*b*). It is clear from lower magnification image that the as-synthesized ZnO are flowerlike clusters in a large-scale area, which are highly disperse in the space without any aggregation and have approximately uniform morphologies. Fig. 2(*b*) shows the higher magnification image of such flowerlike nanostructures, which consist of several symmetric taper arms, composed of a number of aggregative nanorods. Supplementary morphological characterization is achieved through the TEM equipped with the SAED, as shown in Figs. 2(*c*) and (*d*). Fig. 2(*c*) shows the representative TEM micrograph of a typical individual flowerlike ZnO nanostructure. It is worth noting that the branches of the single product grow in different

directions and are composed of symmetric spear-shaped nanorods extending radially from the centre. The diameter of the nanorods in clusters is within 90-100 nm (tip diameter~15 nm) and length of about 2μm. Inset (lower right) of Fig. 2(d) shows a typical TEM image of a single ZnO nanorod to confirm the crystal quality and growth direction. It is clear from TEM image, that the end of the ZnO nanorod is a sharp tip. Furthermore, the HRTEM image (see Fig. 2 (d)) and the SAED pattern (see inset (upper left) of Fig. 2 (d)) are also recorded on a ZnO nanorod. Well-resolved lattice spacing of 0.265 nm corresponding to the *d* spacing of the wurtzite ZnO (0002) plane also indicating that the ZnO nanorod is single crystal in nature and preferentially grows along he [0001] direction (c-axis), which is further confirmed by the SAED pattern. Together with the XRD results and the morphological observations, all these results confirm that the ultra long single-crystalline ZnO nanorods can be fabricated on a large scale by the microwave-assisted aqueous synthesis route.

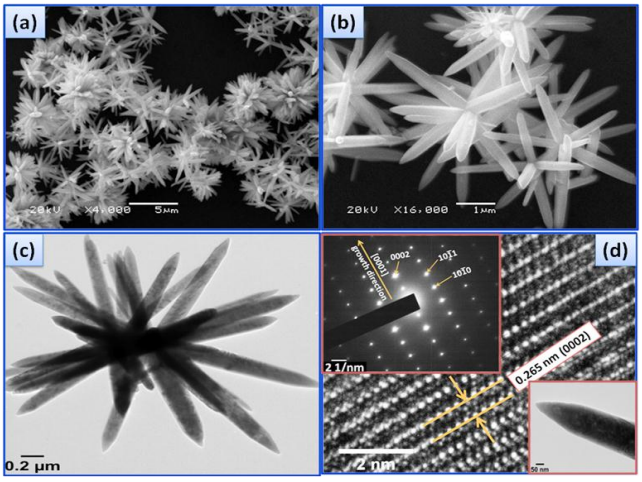

Fig. 2. Morphological description of the aggregative ZnO nanostructures: (*a*) and (*b*) FESEM images at two different magnifications, TEM micrographs of (*c*) an individual ZnO nanoflower and (*d*) HRTEM image of a single nanorod. The upper left and lower right insets in (*d*) correspond to the SAED pattern and the focused image of a single ZnO nanorod, respectively.

The chemical composition of as synthesized ZnO nanorods was investigated by EDX analysis. **Fig. 3** depicts the typical EDX spectrum taken from ZnO nanorods. The chemical analysis of the prepared nanorods measured by EDX analysis shows that only Zn and O signals have been detected, which indicated that the nanorods are indeed made up of Zn and O. No signal of secondary phase or impurity was detected, thus suggested the high purity of ZnO nanorods.

The Raman spectra are sensitive to the crystal quality, structural defects and disorders of the grown products. It is well known that the Wurtzite structure ZnO belongs to the C_{6v} symmetry group. On the prediction of group theory, the existence of the following optical modes at the Γ point of the Brillion zone: $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$. Among them, both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The two nonpolar E_2 modes are Raman active only and the two B_1 modes are infrared. Furthermore, nonpolar E_2 phonon modes have two frequencies. The low frequency E_2 mode (E_2 low) is associated with vibration of the Zn sublattice, whereas the high-frequency E_2 mode (E_2 high) is related to the vibration of oxygen atoms [**30, 31**]. The frequencies of the fundamental optical modes in ZnO reported in the literature [**32**] are : E_2 low = 101 cm^{-1}, E_2 high = 437 cm^{-1}, A_1 (TO)= 380 cm^{-1}, A_1 (LO)= 574 cm^{-1}, E_1 (TO)= 407 cm^{-1}, E_1 (LO)= 583 cm^{-1}, E_2 high_ E_2 low = 333 cm^{-1}.

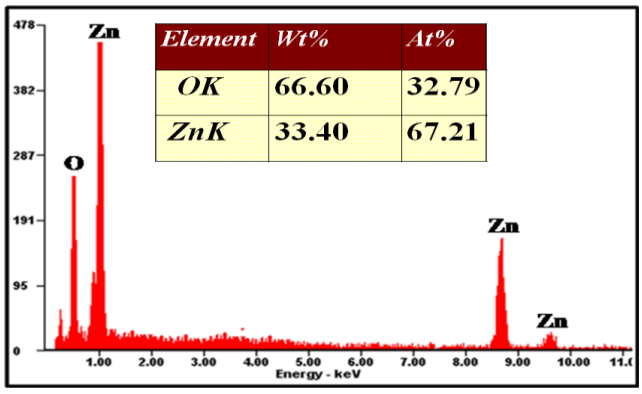

Fig. 3. (Color online) EDX spectrum of the synthesized ZnO nanorods by microwave irradiation.

The typical room temperature Raman spectrum of the ZnO nanorods in the range 100-800 cm^{-1} is shown in **Fig. 4**. The spectrum shows an intense peak at 439 cm^{-1}, which corresponds to the E_2 high mode of the wurtzite ZnO crystal, which is red shifted of ~2 cm^{-1} as compared with the bulk ZnO. The peak at 333 cm^{-1} could be assigned to the second order Raman spectrum arising from zone-boundary phonons E_2 high - E_2 low, while the peak at 386 cm^{-1} correspond to A_1 (TO) phonon modes and found to be red shifted at 6 cm^{-1}. The dominant peak at 583 cm^{-1} is contributed by the E_1 (LO) mode of ZnO associated with the formation of defects such as oxygen vacancies or other defect states. According to the FESEM and TEM results, the large surface area and high surface roughness imply pronounced development of the surface activity compared with that of the bulk crystals and may activate the normally forbidden E_1 (LO) mode.

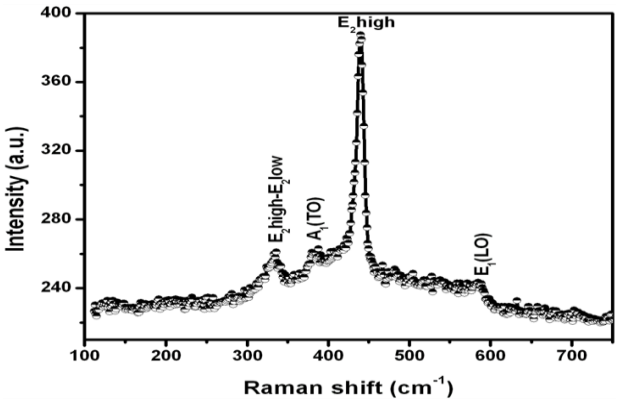

Fig. 4. Raman spectrum of the flowerlike ZnO nanorods.

UV–vis absorption spectrum as shown in **Fig. 5**, is carried out to evaluate the potential optical properties of the as-prepared ZnO nanorods aggregated in flower shape. For the UV–vis absorption measurement, the as-prepared ZnO product is ultrasonically dispersed in absolute ethanol before examination, using absolute ethanol as the reference. The spectrum was corrected for the solvent contribution. The absorption spectrum of ZnO nanorods show well-defined exciton band at ~399 nm (calculated band gap of ~3.10 eV) which is red shifted by ~26 nm relative to the bulk exciton absorption (373 nm) [**33]**. The reason of the shifting of absorption band could be due to the oriented attachment of the nanoparticles by microwave irradiation, may lead to defect formation in the nanorods, which is in good agreement with the Raman studies of the as-prepared nanorods. Similar observations for shifting of absorption bands of ZnO towards visible region were also reported earlier [**34**]. Surface area and surface defects play an important role in the photocatalytic activities of metal oxides. Additionally, it affects the optical and electronic properties [**35**] due to which the optical absorption shifts towards the visible region. For the effective use of ZnO, band gap has to be minimized from 3.38 eV to below 2.0 eV, since it is the recommended band gap value for achieving a visible-light active photocatalyst [**36**]. This is important because of the fact that the solar spectrum has only < 7% UV energy and more than 50% visible energy. However, the pure ZnO phase acts as an efficient photocatalyst only under UV irradiation. One of the strategies adopted for tuning the band gap is to introduce intentional defects in the crystal lattice by which the electronic structure of ZnO can be altered. The defects such as oxygen vacancies are believed to be the centers to capture photoinduced electrons during the process of photocatalytic reactions, which will reduce the recombination rate of photoinduced charge carriers [**36-38].**

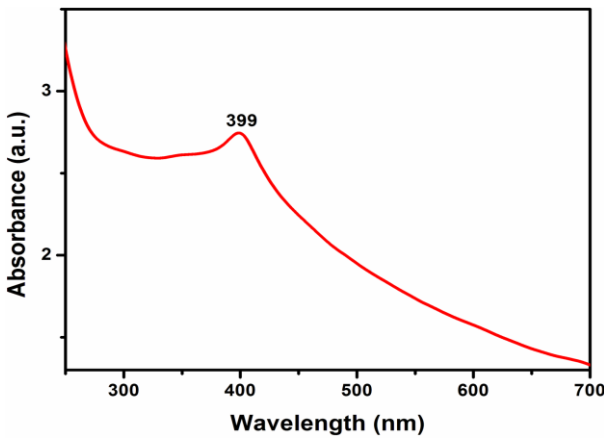

Fig. 5. Room-temperature UV–vis absorption spectrum of as-prepared ZnO nanorods.

Conclusion

In summary, nanocrystalline flowerlike structures composed of hexagonal ZnO nanorods with diameter and length of ~90 nm and ~2 µm, respectively, obtained by FESEM and TEM, have been successfully synthesized by the microwave-assisted aqueous route. The XRD patterns confirmed the formation of wurtzite hexagonal ZnO nanostructures with single phase nature, which is further supported by Raman spectra. The spear shaped nanorods exhibited the UV absorption at ~399 nm. Orient attachment of the nanoparticles by microwave irradiation might lead to defects in the nanorod, which may be the reason for the red-shifted absorption examined by UV–vis absorption spectrum. Due to the advantages of microwave heating with environmental friendly nature, homogeneous and enhanced crystalline nanostructures could be synthesized within a few minutes. This study will provide new approaches to change the optical properties which can be used as a strong tool for future optoelectronic as well as photo catalysis applications.

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